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Synthesis, Characterization and Thermal Behavior of Four Arms Poly(L-lactide) via Ring Opening Polymerization

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Abstract

Four (4-arms, polyL-Lactide) were prepared by having different repeating units (10, 25, 50 and 100) from Erythritols and L-Lactide. The polymers were characterized by several methods as FT-IR, ^{1}HNMR, ^{13}CNMR, Gel Permission Chromatography and Scanning Electron Microscopy and finally their thermal stability was evaluated. The all characterization methods were confirmed the expected structure of prepared polymers, on the other hand the prepared polymers have a thermal stabilizing above 175° C, therefore, it is expected to be suitable for use in tissue engineering and drug release applications.

Keywords: poly L-Lactide, four arms, ring-opening polymerization, thermal behavior.

1. Introduction

The most frequently reported controlled ring-opening polymerization (ROP) of cyclic monomers in the literature (Cabaret et al., 2004; Jérôme and Lecomte, 2008) care coordination-insertion, anionic, cationic, and nucleophilic polymerization. The coordination-inserts and nucleophilic polymerization are undoubtedly the most efficient and general methods reported so far for the ROP of lactones, with cationic and anionic polymerization being much less investigated. The organocatalytic nucleophilic polymerization is a metal-free approach to ROP (Dubois et al., 2009; Cai et al., 2014). Metal-free catalysts, like enzymes and organocatalysts, are attracting growing interest, since being considered to be the more economical and environmentally friendly alternatives (Goldys and Dixon, 2014). The resulting polymers are particularly suitable for biomedical applications, since there is no concern of contamination with metals (Xue and Li. , 2011; Gowda et al., 2011). Furthermore, the polymerization is typically performed at room temperature.

Hedrick et al. reported the catalytic activity of a conjoined thiourea-tertiary amine molecule, in the ROP of lactide (Dove et al., 2005). Mechanics and theoretical studies support a supramolecular bifunctional mechanism involving activation of both the monomer and the alcohol nucleophile; polymerization is significantly slower with reaction times of a few days.

Screening studies demonstrated that a variety of thiourea-amine combinations are catalytically active for the ROP of lactide (.Pratt et al., 2006). The step acceleration of polymerization attributed to the higher basicity of (-)-sparteine compared to the tertiary amine (Lohmeijer et al., 2006) to use even stronger organic bases, so-called superbases, such as the amidine 1,8-diazabicycloundec-7-ene (DBU), guanidine 1,4,7-triazabicyclodecene (TBD), and N-methylated TBD (MTBD).

1,8-diazabicycloundec-7-ene (DBU) catalysed ROP of L-lactide was tested in $CDCl_3$ at room temperature using 100:1:1 monomer/catalyst/initiator (1-pyrene-butanol, Py Bu) ratio suggested by Pratt et al. The resulting polymer was found to have mean Mn 21,000 g/mol and polydispersity (PDI = Mw/Mn) equal to 1.05. Sampling of a polymerization reaction showed a linear increase of Mn with conversion while the PDI stayed close to 1.05, even at conversions up to 99%. The molecular weight of the poly(lactide) could be controlled by varying of the monomer/initiator ratio of 50:1 to 500:1 with good correlation of the targeted and experimental Mn values, again with PDI < 1.1.

Soeh (2014) reported a synthesis of novel triblock copolymers of poly (L-lactide)-poly(ethylene glycol) sebacate-poly (ethylene glycol)-poly(L-lactide) were synthesized by Ring-Opening Polymerization (ROP) using (DBU) as a catalyst and different ratio of L-lactide with three pre-prepared poly(ethylene glycol) sebacate-poly (ethylene glycol) polymers. Qian, et al. (2011) used (DBU), a known, effective, and convenient organocatalyst for the ring opening polymerization of cyclic esters, to synthesize random copolymers of lactide and glycolide. Cheuma, et al. (2008) recommended two mechanisms for the ROP of L-lactide using a guanidine-based catalyst, the first involved acetyl transfer to the catalyst, and the second involving only hydrogen bonding to the catalyst, they found out that the hydrogen-bonding pathway was considerably preferred over the acetyl transfer pathway and that was consistent with experimental information.

2. Materials

L-Lactide, Pentaerythritol, Diazabicyclo [5.4.0] undec-7-ene (DBU) and Magnesium sulphate were supplied by

(Sigma-Aldrich Co.), Dichloromethane (DCM) (Assay ≥ 99.5 %) and dimethylformamide (DMF) (Assay ≥ 99.8 %) were supplied by MACRON Company

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3. Instruments

The FTIR spectra were recorded using Nicolet IR-42, Mid-IR spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded using Agilent DDR2 500MHz NMR spectrometers available at Department of Chemistry/Michigan State University.

Polymers molecular weights and molecular weight distributions (Mw/Mn) were determined using a Waters 1515 gel permeation chromatography (GPC) equipped with a refractive-index detector (Waters 2412), DMF was used as the eluent at a flow rate of 1.0 mL/min and calibrated with poly(methyl methacrylate) standard, which is available at Department of Chemistry/Michigan State University.

Computer controlled thermal analysis Instrumentals, TGA-Q500 V20.10 was used, it is available at Centre for Composite Materials and Structure/Michigan State University.

4. Preparation of (Pentaerythritol-lactide) Polymer (Polymer PL_{10})

Pentaerythritol (0.4084 g, 0.003 mole) and L-Lactide (8.6478 g, 0.06 mole) were dissolved in DMF (25ml) at room temperature. After stirring for 5 minutes under nitrogen atmosphere, DBU (90 µl) was added into the mixed solution. The reaction was kept under nitrogen for 2 hours. The reaction was stirred for a further 24 hours at room temperature. Afterwards, the reaction was worked up by the slow addition of the reactants to 500 ml cold distilled water to precipitate the polymer which was then filtered on a Buchner funnel and washed with distilled water and then the filtrate was dissolved in DCM (25ml) and dried over anhydrous magnesium sulphate and filtered. The polymer was recovered through the column chromatography with silica gel, DCM was removed by rotary evaporator and the polymer was dried in vacuum oven at 25^{o}C for 24 hours. (Yield 66%).

The same procedure was carried out to prepare polymers PL_{25}, PL_{50} and PL_{100}, Table 1 lists the quantities of reactants used in the preparation and the chemical equations can be represented by Scheme (2.1) of these polymers.

Table 1: The quantities of reactants used in the preparation of PL_{25}, PL_{50} and PL_{100} polymers

Polymer Code	Amount of pentaerythritol		Amount of L-lactide		DBU (µl)	Yield (%)
	Weight (g)	No. of moles	Weight (g)	No. of moles		
PL_{25}	0.1634	0.0012	8.6478	0.06	90	72
PL_{50}	0.0817	0.0006	8.6478	0.06	90	77
PL_{100}	0.0545	0.0004	11.5304	0.08	120	88

5. Results

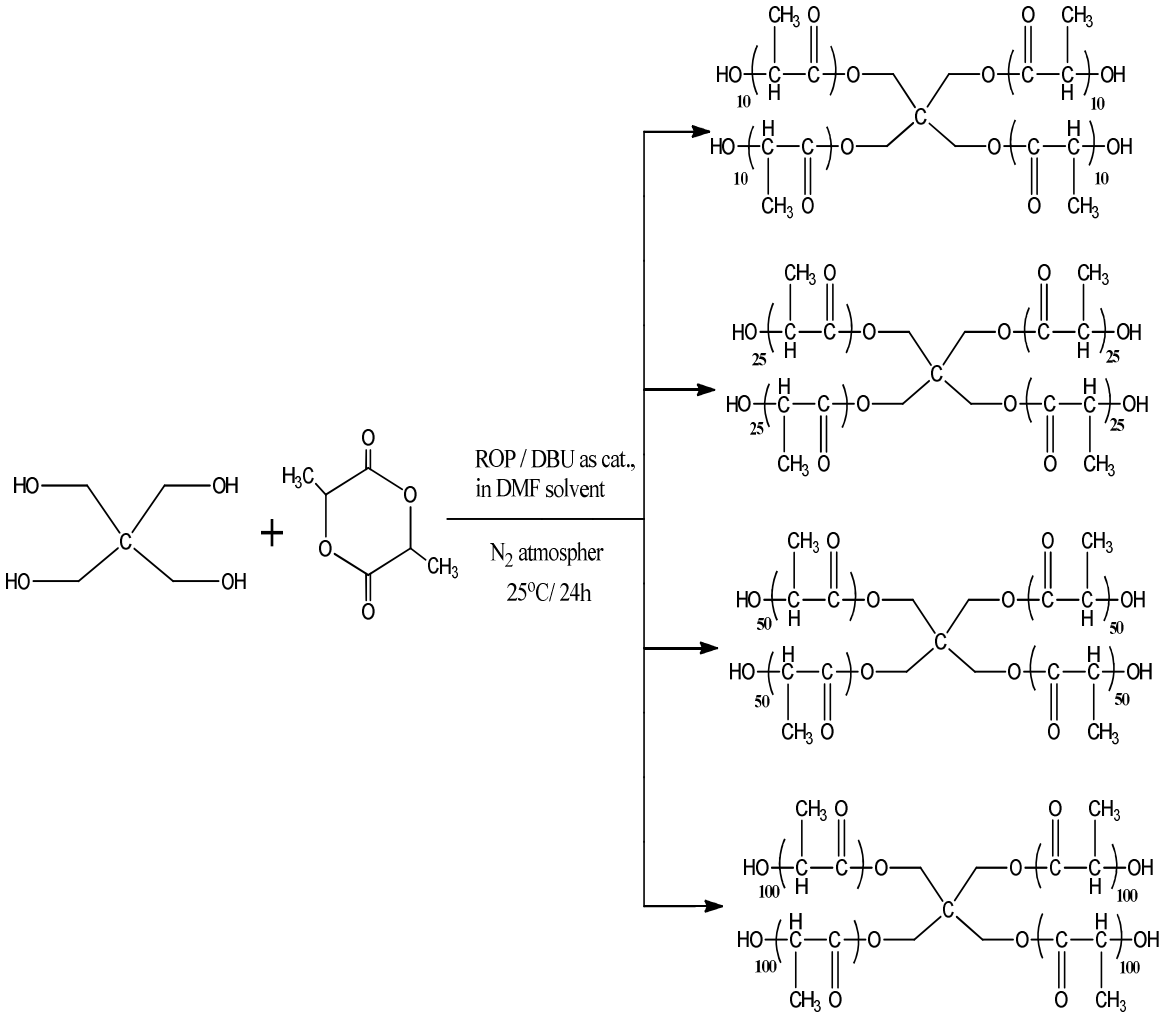
5.1 Characterization of (Pentaerythritol-lactide) polymers (PL_{10}, PL_{25}, PL_{50} and PL_{100})

5.1.1 Characterization of new polymer by FT-IR

The viscous prepared polymers were characterized by put a small amount of the viscous polymer on KBr disc, and the solid prepared polymers were characterized as KBr discs. Figure 1 represents IR spectra for these prepared polymers.

5.1.2 Characterization of new polymer by NMR

^{1}H NMR and ^{13}C NMR techniques were used to confirm the structure of the new prepared polymers (PL_{10}, PL_{25}, PL_{50} and PL_{100}) and Figures (2 and 3) represent ^{1}H NMR and ^{13}C NMR spectra for these prepared polymers.



Scheme 1: Chemical equation of preparation the polymers PL_{10}, PL25, PL50 and PL_{100} by ROP to L-Lactide with Pentaerythritol

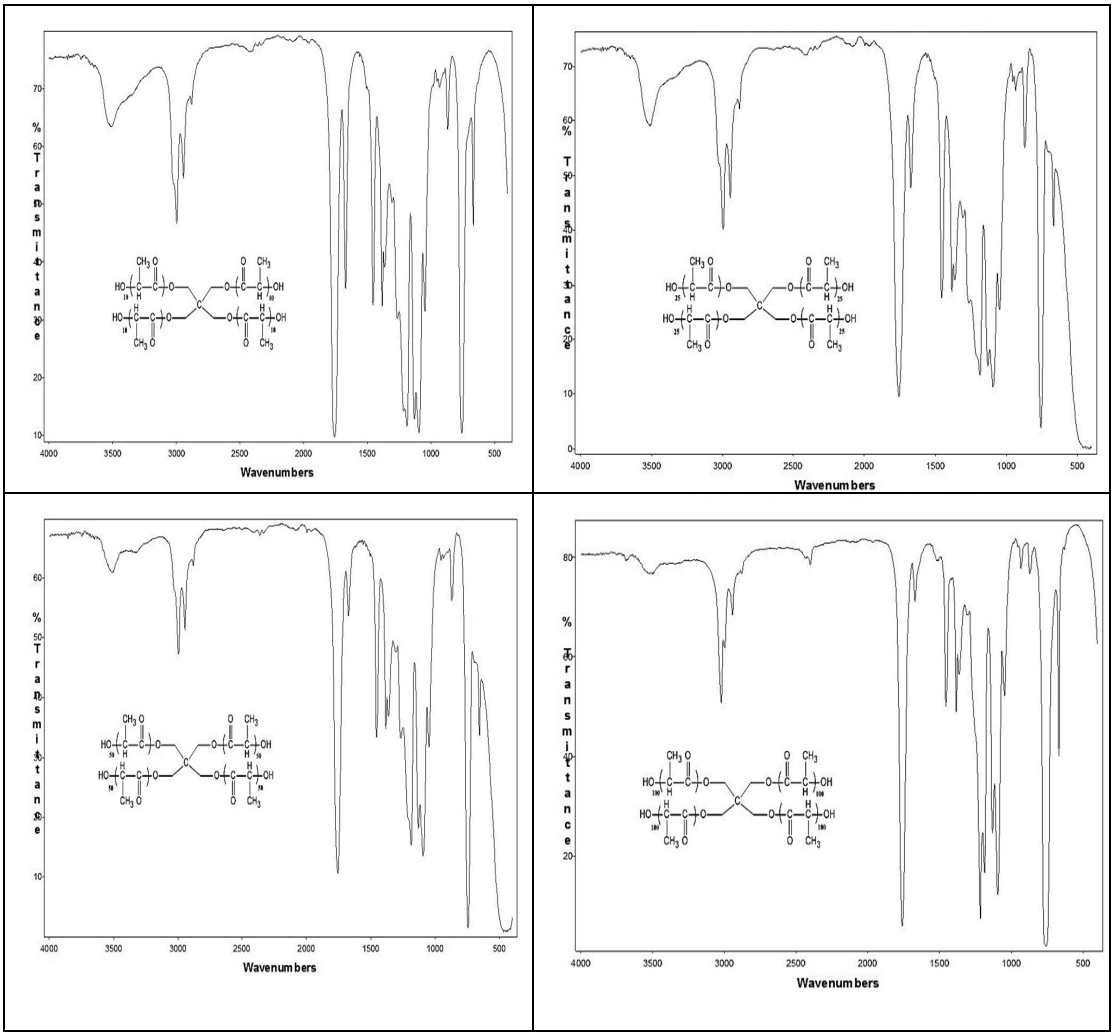


Figure 1: FT-IR spectra of PL_{10}, PL_{25}, PL_{50} and PL_{100}

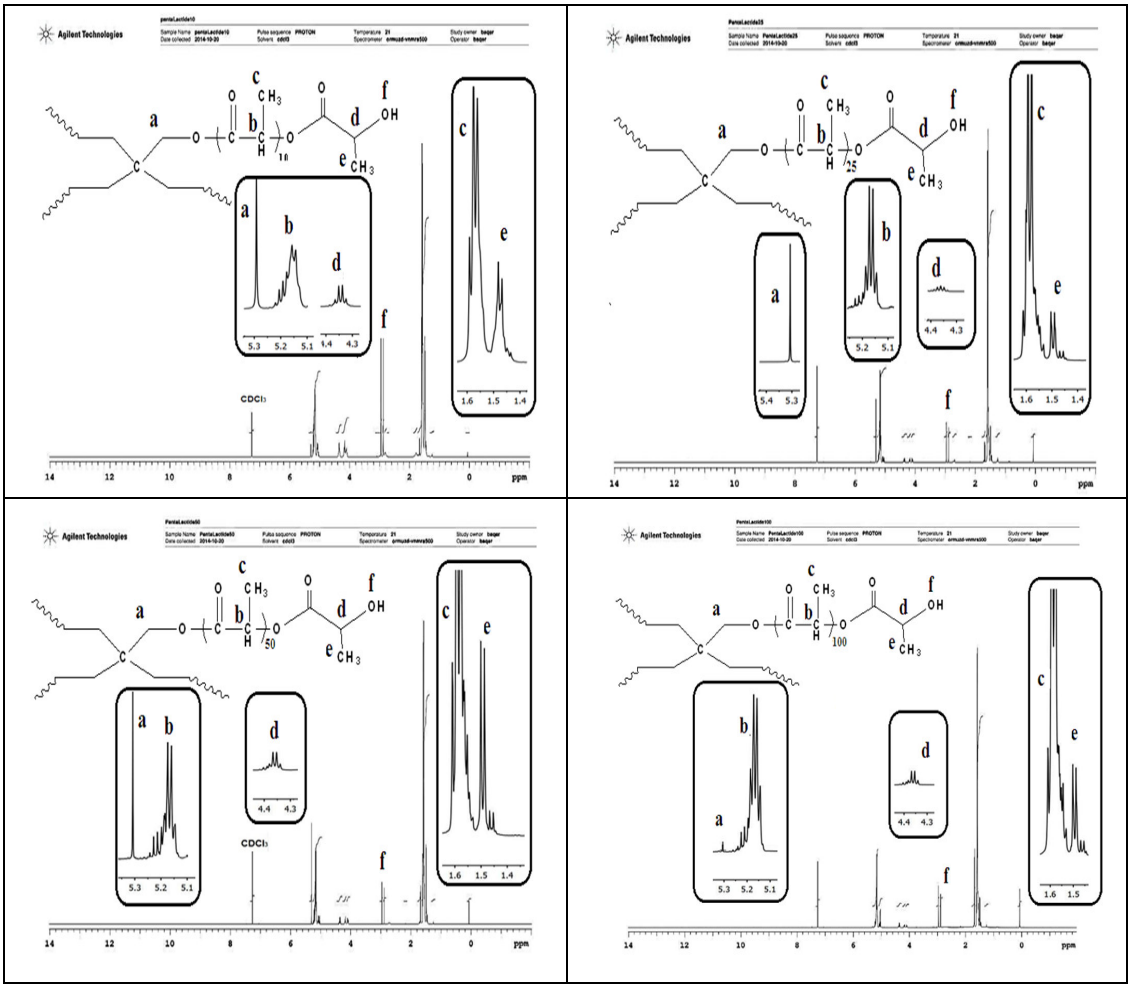


Figure 2: ^{1}H NMR spectra of PL_{10}, PL_{25}, PL_{50} and PL_{100}

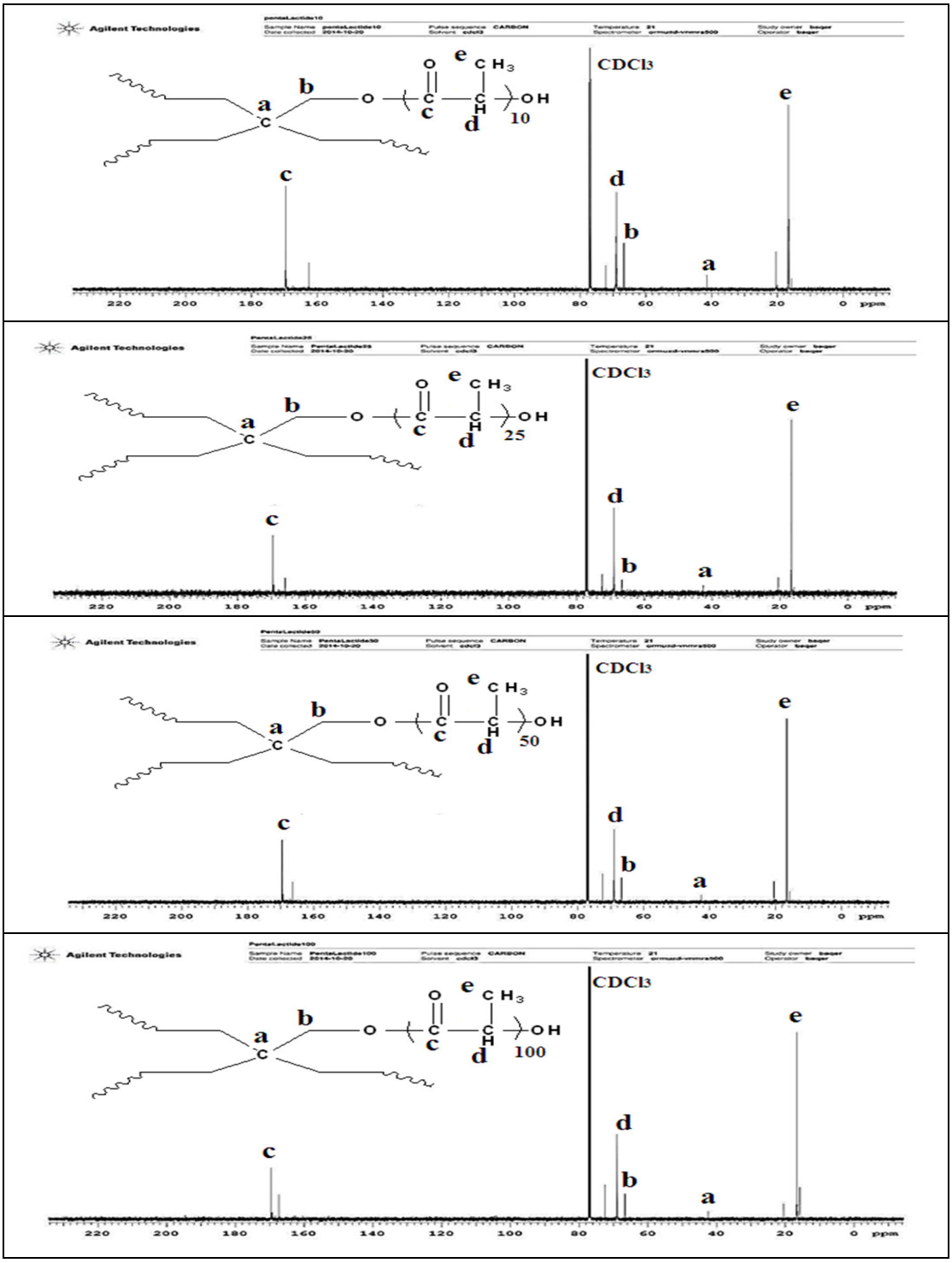


Figure 3: ^{13}C NMR spectra of PL_{10}, PL_{25}, PL_{50} and PL_{100}

5.1.3 Determination of polydispersity index by Gel Permeation Chromatography (GPC)

The molecular weight distributions (Mw/Mn) were determined for all prepared polymers and Table 2 shows the GPC results.

Table 2: GPC results for prepared polymers

No.	Polymer Name	Calculated M_n (Daltons)	Found M_n (Daltons)	Found M_w (Daltons)	Polydispersity Index (PDI)
1	PL_{10}	3018	3063	3317	1.082927
2	PL_{25}	7342	7319	8351	1.141007
3	PL_{50}	14549	14563	15805	1.085304
4	PL_{100}	28962	28903	31102	1.076091

5.2 Thermogravimetric Analysis (TGA)

Thermal stability of the prepared polymers was studied and Figure 4 shows the resulted thermograms. Table 3 shows some thermal functions resulted from the thermal analysis like initiation and final decomposition temperatures T_i and T_f , rate of decomposition, the activation energy of the decomposition, 50% weight lose temperature (T_{50}) and char content.

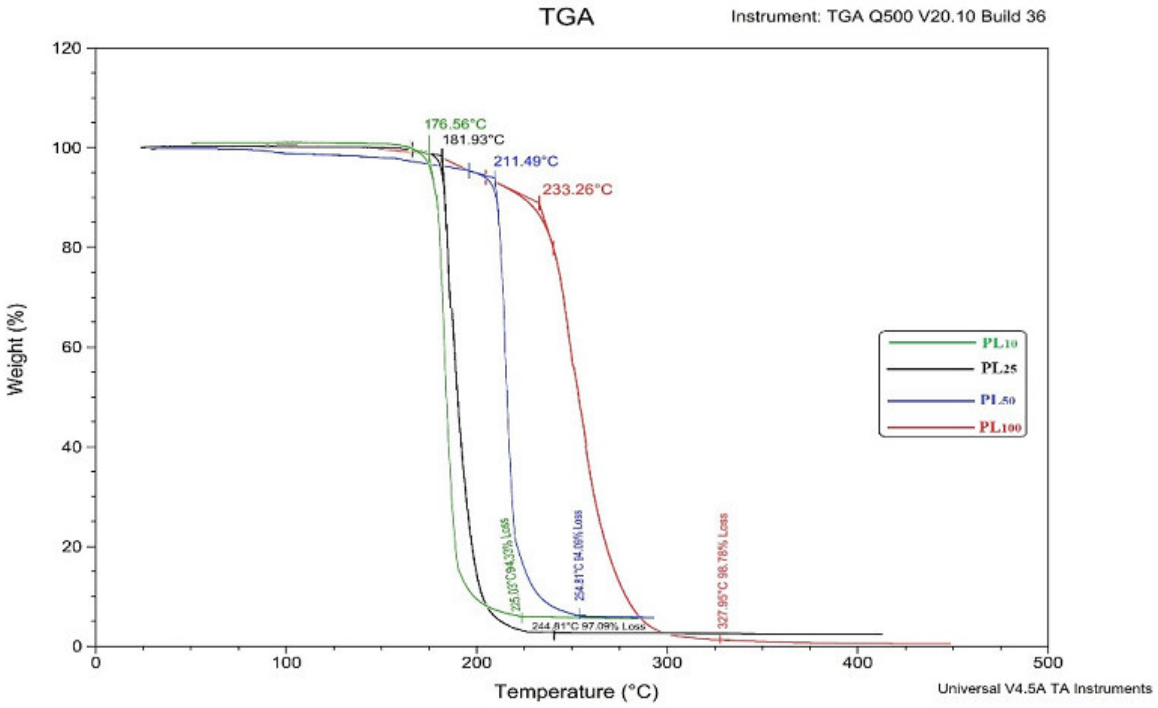


Figure 3: Thermogram of PL_{10}, PL_{25}, PL_{50} and PL_{100}

Table 3: TGA data for Pentaerythritol-lactide polymers (PL_{10}, PL_{25}, PL_{50} and PL_{100})

Polymer	T_i (^oC)	T_f (^oC)	Rate of Decomps. % wt / min	Activation Energy kJ.mol^{-1}	Char content (%)	T_{50} (^oC)
PL_{10}	176.56	225.03	6.33	0.011	5.67	186.03
PL_{25}	181.93	244.81	3.96	0.013	2.91	190.60
PL_{50}	211.49	254.81	3.21	0.013	5.91	215.94
PL_{100}	233.26	3027.95	1.95	0.026	1.22	253.57

6. Discussion

The FT-IR spectra were clearly shown the presence of hydroxyl groups υ(cm-1) 3506-3517 cm^{-1}. The ^{1}HNMR spectra shows peak to the methylene protons in (CH_2) group of pentaerythritol at 5.3 ppm, the peaks at around 5.2 ppm represented to the methylene protons (CH) of repeating unit of L-lactide segments and at 1.6 ppm represented to methylene (CH_3) protons of repeating unit. The peak at 4.4 ppm and 1.5 ppm for the methylene protons (CH) and (CH_3) of terminal repeating unit of L-lactide respectively, and finally the peak at 2.9 ppm for hydroxyl groups at the end chains of polymers while the ^{13}C NMR spectra shows the centre carbon atom of pentaerythritol were around 41 ppm, the peaks at 67 ppm represented to the carbon atom in a methylene group of pentaerythritol, and at about 170 ppm represented the carbon atom in the carbonyl group of repeating unit of L-lactide. The peak at 69 ppm for the carbon atom of the methylene group of repeating unit of L-lactide and at 17 ppm represented the carbon atom in methylene group (CH_3) of L-lactide. All these results confirmed is the expected structure and composition of the prepared polymers and promoted this matter with great accuracy the results of GPC as shown significant closely with theoretical calculations of molecular weight and result the awesome polydespersity index (PDI) is close to one.

Thermal gravimetric analysis indicates that the initial decomposition temperature (T_i) ranging between (176-233) ^{o}C. Table 3 indicates that the initial decomposition temperature for prepared polymers were increased with increasing of repeating units of lactide and the rate of decomposition were decreased with increasing of repeating units ,this is an expected result because with increasing molecular weight of the polymers will increase the thermal stability. The thermal stability results indicate the possibility of using these polymers in tissue engineering and drug delivery applications.

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